Exploring the possibility of *Polyalthia longifolia* (False Ashoka) plantation as air quality mitigation at kerbside locations

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Certificate of Examination

This is to certify that the dissertation titled "Exploring the possibility of Polyalthia longifolia (False Ashoka) plantation as air quality mitigation at kerbside locations" submitted by Mr. Parkar Vidit Suryakant (Reg. No. MS15041) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Baerbel Sinha (Supervisor)

Dr. Anoop Ambili

Dr. Raju Attada

Dated: 4, May, 2020

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Baerbel Sinha at the Indian Institute of Science Education and Research Mohali.
This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Parkar Vidit Suryakant
(Candidate)

Dated: 4-5-2020

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Baerbel Sinha
(Supervisor)

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I want to thank my parents for their constant support in my life. I thank my thesis supervisor has guided me through this early academic career phase of my life. I would also like to acknowledge the informal guidance by Dr. Vinayak Sinha, who inspired me to push the boundaries of my knowledge. IISER Mohali along with INSPIRE-SHE has given me a platform to explore my interests and I feel lucky to be studying and working here.

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Notation (abbreviations)

SM	Soil moisture
VPD	Vapour pressure deficit
PAR	Photosynthetic active radiation
BVOC	Biogenic volatile organic compound
NW-IGP	Northwest Indo-Gangetic Plane
PM	Particulate matter
CVC	Crown volume coverage
MFCs	Mass flow controllers
SWP	Soil water potential
RH	Relative humidity

CONTENTS

Abstract

Urban forestry has been promoted under the Agenda 21 (United Nations, 1993) as a means to make cities more sustainable and carbon friendly (Churkina et al. 2015). This works primarily through three pathways, which we explore using *Polyalthia longifolia* (False Ashoka), a tree that accounts for 5-20% of the urban plantations in Indian cities. Firstly, trees sequester carbon directly. A *Polyalthia longifolia* tree with approximately 3-4 cm stem diameter at breast height and a height of 3 meters (i.e. a relatively small tree trimmed for aesthetic purposes) has a canopy area of 0.9-1 m^2 and a LAI of 0.8 and sequesters around 8000 kg of CO_2 per year. However, the second and more important mechanism through which trees in hot climate contribute to making cities less carbon intensive, is, by cooling their surrounding through evapotranspiration. The same tree evaporates approximately 640,000 kg of water thus cooling its surrounding. This reduces the energy expenditure for space cooling. Thirdly, trees adsorb particles and trace gasses through the process of dry deposition. One such tree sequesters 9.6 kg of ozone per year.

In this study we calibrated the DO_3SE stomatal ozone uptake model for *Polyalthia longifolia.* Just like other tropical evergreen trees the tree shows maximum stomatal conductance during wet seasons but has a remarkable capability to keep up photosynthesis even at high temperatures and Vapor pressure deficits in summer. Such extreme tolerance to dry conditions has not been reported so far for any species and may be related to the tree tapping into the groundwater via a single tap root. As the stomatal conductance of this tree peaks in the early morning hours it has a strong capability to sequester other criteria air pollutants, in particular NO_2.

Chapter 1

Introduction

1.1 The role of roadside vegetation for mitigating heat, noise and particulate matter mass loadings – a literature review

Urban forestry has been promoted under the Agenda 21 (United Nations, 1993) as a means to make cities more sustainable and carbon friendly (Churkina et al. 2015). This works primarily through three pathways. Firstly, trees sequester carbon directly. However, the second and more important mechanism through which trees in hot climate contribute to making cities less carbon intensive, is, by cooling their surrounding through evapotranspiration. This reduces the energy expenditure for space cooling, which contributes significantly to the total energy consumption of buildings in hot countries. Globally buildings consume 21% of our carbon footprint. Thirdly, trees adsorb particles and remove them from the atmosphere through the process of dry deposition (Islam et al. 2012) and take up criteria air pollutants (NOx, SO_2(g) and NH3(g)) through their stomata and hence reduce the formation of secondary nitrate, sulphate and ammonia aerosols. As NOx is an important precursor of tropospheric ozone, which is a greenhouse gas and black carbon from diesel vehicles contributes significantly to the particulate matter burden in cities, kerbside trees could actually be reducing the tropospheric abundance of short lived climate forcers. At the same time, they emit volatile organic compounds (VOCs). Certain VOCs such as terpenes promote the formation of secondary organic aerosol (SOA) and can fuel the formation of secondary pollutants such as ozone. The net impact of trees on urban air quality is till date far from clear and likely depends strongly on the species planted.

Many countries have started fast-track programs to plant trees in cities. These programs aim at the reducing of summer temperatures, increasing carbon storage, improving storm water control and providing green space for recreation. Such program are also a tool for poverty alleviation when they include community garden spaces or plantation of fruiting species from which the fruits are free to plug for all (Churkina et al. 2015). The selection of species for these programs, however, has often been done by civil planning authorities that are unaware of the role trees play in the formation of secondary pollutants such as particulate matter and ozone. Particulate matter and tropospheric ozone have an adverse impact on human health. They can worsen the prognosis for patients of asthma, chronic obstructive bronchitis and those with cardio-vascular related ailments. They have also been implicated in causing cancer and low birth weight babies and premature deliveries (Vailshery, Jaganmohan, and Nagendra 2013).

In general, the capability of trees to remove pollutants is directly proportional to the dry deposition velocities of the pollutant in question. Overall most studies find the larges reduction occur for PM_{10} (aerosol particles with an aerodynamic diameter of less than 10 μm), that is large particles which have a high terminal fall velocity and collide easily with the leaf surface. One study estimated that Beijing's tree remove an estimated 1200 tons of air pollutants from the city in 2002 (Vailshery et al. 2013). Observation based on a statistical model indicated that temperature and wind direction influenced PM10 removal rates (Yin et al. 2011). The relationship with wind direction can be easily understood as it modulates how much of the particulate matter suspended on the road moves towards the trees planted along the road side. The relationship with temperature may be a coincidence due to the fact that temperature, boundary layer height and the ventilation coefficient are often connected. Yin et al., 2011 reports that as crown volume coverage increases, total suspended particles' removal rates would increase faster than gaseous pollutant removal rates with an increase in tree cover. Some studies also showed that too dense vegetation would cause changes air turbulence and decline the vegetation health (Islam et al. 2012) and that a multi storeyed canopies with trees of different heights, shrubs and ornamentals are more efficient that tree monocultures in sequestering pollution. Overall most studies suggest that the net impact of urban trees is that of pollution removal rather than that of secondary pollution formation, however, the majority of the studies available at present consider either only the pollution formation potential or only the pollution removal capability. Studies looking at both aspects in an integrated manner for the same species are sorely lacking. In addition to their favourable impact on primary pollutants, greenbelts reduce noise at kerbside locations by 13-17dB (Islam et al. 2012). The maximum attenuation depends on the species and was found to be 17 dB for *Putranjiva roxburgi* and 14 dB for *Cestrum nocturnum* (Islam et al. 2012). In general, the same structural properties in terms of crown structure, leaf structure and crown density, that make trees efficient in acting as a dry deposition sink for primary pollutants also make them good in attenuating noise pollution, hence noise and air pollution mitigation are easy to reconcile while selecting trees for urban plantation.

Unfortunately, during the plantation process, the selection of species is often guided by ecological considerations, the economic value of the tree, aesthetic purposes and the amount of maintenance work the trees generate for the municipality without factoring in whether trees contribute towards urban cooling during the hot and dry summer season when it is most needed. Winter deciduous trees that could allow urban heating to occur in winter when it reduces energy consumption but prevents it from occurring in summer, are often avoided by authorities unwilling to deal with the leaf litter. Significant temperature control through trees was illustrated in Bengaluru with ambient air temperature in road segments with trees are reported to range from 23.1-34.2 ºC and without trees 23.4–38.3 ºC (Vailshery et al. 2013). While there is little difference between segments with and without trees for the night time temperature low, a significant difference is observed for peak daytime temperatures making urban trees an important tool to mitigate heat stress exposure of the urban poor and of outdoor workers. As a consequence, they provide tangible economic benefits by reducing heat related mortality and morbidity of the urban population and enabling outdoor workers to carry out their activities for longer. Hence they increase workers' productivity. The higher air temperatures in urban areas and the large fraction of sealed surfaces that prevent infiltration of rainwater as well as the high kerbside pollutant concentrations significantly stress urban vegetation (Islam et al. 2012). Species selected for plantation must be capable of dealing with such stresses and should also have root structures that do not interfere with civil infrastructure. All these considerations related to the capability of the tree to grow under the aggravated conditions and its tendency to interfere with the structural safety of buildings through its root systems severely limit the number of species that can be considered for urban plantation and result in a situation where the impact of the selected tree on secondary pollutant formation and its summertime cooling potential are often neglected while making a plantation decision.

1.2 The role of roadside vegetation as a sink for trace gasses such as NOx, SO2, O3 and NH3– a literature review

Roads act as strong NOx line sources as the transport sector, industries and power plants are the most important sources of NOx globally. When NOx emissions are mixed with emissions of volatile organic compounds and the air mass ages, rampant production of a secondary pollutant ozone can occur (Churkina et al. 2015). Since the sulphur content of vehicular fuel is tightly regulated as part of the Bharat Stage IV and now VI fuel standards, thermal power plants, backup generators and industrial boilers that use cheap sulphur rich oil are major sources of anthropogenic SO_2 in the urban environment. Dry deposition onto vegetation surfaces is a very efficient mean to reduce SO_2 mixing ratio year around. However, the dry deposition of acidic trace gasses such as sulphur dioxide and oxides of nitrogen to the surface of leaves can be very harmful to trees in the long run as the same get oxidised to acids on the surface and fall to the ground during the next rain event. This can result in extremely acidic (pH <2) throughfall (rain that has fallen through the crown of a tree) even at sites where the rainfall pH is higher (~pH 4.5). This acidification of throughfall has been a major cause behind tree mortality in North America and Europe in the 1970's and 1980's that became a trigger for air pollution mitigation and the convention on the long range transport of air pollution (CLATRAP). Fortunately, in India the acidic trace gasses are often neutralized by ammonia. Urban air pollution levels, can be mitigated cost-effectively by urban green spaces as their presence increases the dry deposition sink of O_3 and its precursor (NO_x) (Sicard et al. 2018). Most highly acidic or alkaline trace gasses such as NO_2, SO_2 and NH_3 have high deposition velocities for grasses and broadleaf species (0.2-0.4 cm s^{-1}) (Pugh et al. 2012). O_3 deposition velocities vary from 0.06 to 1.8 cm s^{-1} (Pugh et al. 2012) and are generally high when stomatal conductance is high. The removal rate on SO_2 and NO_2 increases by 15% and 20% respectively as the crown volume coverage (CVC) increases from 0 to 2 (Yin et al. 2011). Vailshery et al., 2013 reports 14 µg m^{-3} lower ambient SO_2 on roads with roadside vegetation compared to roads without roadside vegetation. Various models exist to estimate dry deposition of O_3 on vegetation, one of them is DO_3SE dicussed in further sections. Dry deposition of NH_3 on vegetation is estimated with several models but large deviations exist between these models.

Vegetation condition including the response of stomatal conductance to water vapour pressure deficit, soil moisture, temperature and solar radiation, crown structure and leaf area index and pollutants diffusion distance are among the key factors to affect pollutant removal rates (Yin et al. 2011).

1.3 The role of roadside vegetation as a source of ozone precursor emissions and the impact of species selection on secondary pollutant formation

Biogenic volatile organic compounds (BVOCs) are emitted by plants through a variety of mechanism and for several purposes. In general, their emission depends on light, and temperature. Most plants emit more BVOCs when they are stressed or under attack by pathogens or herbivores (Calfapietra et al. 2013). Isoprenoids are emitted as a by-product of photosynthesis and may play a role in protecting plants against heat stress. As large urbanized areas are usually subjected to the "Urban Heat Island" (UHI) effect the emission profile of roadside plants may differ from that of plants grown in natural environments. Moreover, road side locations are also often exposed to significantly elevated CO_2 levels that may impact the emissions from plants (Calfapietra et al. 2013). While some VOCs emitted from tailpipes and fires such as benzene, or polycyclic aromatic hydrocarbons have negative impacts on human health and are known to be carcinogens (Bonn et al. 2018), the terpenoid compounds most abundantly emitted by plants are not known for adverse impacts on human health. However, in the NOx rich urban environment highly reactive BVOC's namely isoprene, terpenes and sequiterpenes can readily contribute to tropospheric ozone formation and secondary organic aerosol (SOA) formation. Isoprene has high reactivity, low atmospheric lifetime (<2 hrs). It oxidizes to methyl vinyl ketone (MVK) and methacrolein (MACR) in the first step. Its complex gas phase oxidation mechanism has more than 4000 reactions and results in the formation of hydroxyhydroperoxides (ISOPOOH), and formaldehyde (HCHO)(Mo et al. 2018).

Tropospheric ozone is a criteria air pollutant. It has been established that high levels occur in the presence of elevated levels of (a) sunlight, (b) nitrogen oxides and (c) volatile organic compounds (VOCs).

90% of our planet's ozone is in the ozone layer in lower stratosphere that ozone is called the good ozone as it shields all living things from exposure to too much UV radiation. The troposphere has relatively less ozone, but its presence is to humans and plants at a sustained exposure of 40 ppbv or higher. Human exposures to O_3 results in increased numbers of hospital admissions and premature mortality. As it causes significant oxidative stress in the lungs and the whole organism, tropospheric ozone worsens the prospect for many respiratory conditions such as asthma and pneumonia and cardiovascular diseases. It reduces worker productivity and increased medication use for certain conditions that are modulated by oxidative stress in the organism (Sicard et al. 2018). In India, National Ambient Air Quality Standards are prescribed by Central Pollution Control Board to regulate various air pollutants. According to NAAQS the prescribed primary and secondary levels for ozone are 100 µg/m^3 (8 hours) and 180 µg/m^3 (1 hour) [50 ppbv (8 hours) and 90 ppbv (1 hour)] respectively at NTP(USEPA 2014).

Tropospheric ozone, as suggested by Blacet (1952), is produced by photolysis of NO_2 following the reactions below:

$$NO_2 + h\upsilon\ (\lambda \leq 430nm) \rightarrow NO + O(^3P)$$

$$O_2 + O(^3P) + M \rightarrow O_3 + M$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

The above ozone formation process is a null cycle. This null cycle is broken whenever any molecule other than ozone converts NO to NO_2. As a consequence, reactive VOCs play important role to play in tropospheric ozone formation.

VOCs are generally oxidised by the OH radical. In the first step the reaction forms organic peroxy radicals (RO_2). These radicals can convert NO into NO_2. Every time NO is converted to NO_2 by a species other than ozone the reaction results in net ozone formation. The same reaction also results in the formation of a hydroperoxy radical (HO_2) which can again with NO and convert it to NO_2. A by-product of the reaction is the formation of another OH radical. Hence, under certain conditions, isoprene oxidation can result in recycling of OH radical. Therefore, highly reactive hydrocarbons such as isoprene (C_5H_8) will enhance the ozone production.

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$$

$$R^{\bullet} + O_2 + M \rightarrow RO_2 + M$$

$$RO2 + NO \rightarrow RO^{\bullet} + NO2$$

$$RO^{\bullet} + O2 \rightarrow RCHO + HO2$$

$$HO_2 + NO \rightarrow NO_2 + {}^{\bullet}OH$$

Second, VOCs can react with ambient oxidants such as ozone and form larger products. Larger terpenes are known to undergo ozonolysis and the reaction produces secondary organic aerosol (Bonn et al. 2018).

In a kerbside environment, the cycle typically starts with the emission of NO from the tailpipe. As a consequence, the ozone mixing ratios near a road can be very low, in particular, when there is no vegetation nearby. This is called the NO titration of ozone. Planting roadside vegetation can change this situation. NO and NO_2 are in a photo stationary state and the interconversions between the two occur so fast that the timescales are shorter than the timescales on which street canyons are ventilated at the average wind speeds in many places. Adding vegetation with a strong BVOC emission potential to a kerbside location, can fuel ozone formation not only downwind, but within the urban environment. With a high isoprene or terpene emissions within meters of the tailpipe, species other than ozone can convert NO to NO_2 resulting into a net ozone formation even within cities. As a consequence, urban air quality in India could improve if urban planners would factor in the secondary pollution potential of the selected species and would maximize for pollution sequestration while minimizing the emission of ozone and aerosol precursors by virtue of selecting the right species.

1.4 The Novel of the study

So far most studies have considered either the impact of plants on pollution sequestration via primarily changing dry deposition velocities or the impact of plants on ozone and SOA precursor emissions. In this study we quantify both the precursor emission potential and the air pollution mitigation potential of the same plant. Achieving an enhancement in pollutant deposition has received little attention in most developed economies (Pugh et al. 2012) but is widely used as air and noise pollution mitigation instrument in India and other South Asian countries, where the beneficial effects of roadside tree plantation were recognized early on. Since roadside plantations are widespread, improving their structure and composition so that pollution mitigation is maximized and secondary pollution formation is minimized could improve urban air quality substantially. This study attempts to quantify the ozone uptake and emission of ozone precursors for *Polyalthia longifolia* using field based measurements. Uptake of ozone is calculated using a simple multiplicative model for dry deposition of ozone (DO_3SE) on trees. The output of the same model can be used to also calculate the uptake of precursors such as NO and NO_2 and other criteria air pollutants such as SO_2 and CO. The DO_3SE model is based on the exchange of water vapour through the stomata of leaves. Stomata aperture is mainly regulated five functions: phenology, PAR, temperature, soil moisture and VPD. The emission flux of BVOCs was measured with dynamic branch cuvette and PTR-QMS. Polyalthia longifolia is being preferred many densely populated cities, such as Bengaluru, for its relatively smaller canopy size(Vailshery et al. 2013). Here we are exploring the potential of Polyalthia longifolia in air pollution mitigation.

1.5 Deposition of Ozone for Stomatal Exchange (DO_3SE) Model

DO3SE model stands for deposition of ozone for stomatal exchange. DO_3SE model has been accepted as the most appropriate tool to quantify the impact of pollution on plants and the damage induced by the EMEP LRTAP Convention in 2007 (Simpson et al. 2007) as a tool to assess the impact of ozone pollution on various economically important plants such as rice, wheat, pulses and potatoes and for quantifying the pollution damage of natural vegetation. This model helps in calculating the stomatal flux of ozone into the plant. The uptake of ozone from the air into the plant can be modulated by stomatal aperture, which the plant regulates primarily to control photosynthesis and respiration and control moisture loss. Hence a high concentration of ozone in the air does not automatically result into a high ozone uptake by the plant if it happens to occur at a time when the air is hot and dry. Those plants that are capable of minimizing moisture loss by closing their stomata to preserve moisture will take up less ozone from the air under such circumstances. Hence the stomatal ozone flux is a much better proxy for ozone uptake by a plant than its ambient air concentration. The DO3SE approach for stomatal resistance modelling is based on a multiplicative stomatal conductance model which was first described by Jarvis (1976) and has been modified by Korner et al (1995). A ready to use software was built by Lisa Emberson. The software can be customized to provide the species specific stomatal conductance by adjusting response functions that express stomatal conductance as a fraction of g_{max} is the species specific maximum stomata conductance to ozone (mmol m^{-2} s^{-1}) expressed in mmol per m2 of total leaf surface area per second. All parameters are expressed as the modification of g_{max} to the above mentioned factors. Phenology function tends to peak during the vegetative growth season.

$$G_{sto} = g_{max} * g_{pot} * max\{g_{min}, (g_{light} * g_{temp} * g_{VPD} * g_{SWP})\}$$

$$f_{temp} = max\{f_{min}, [(T - T_{min})/(T_{opt} - T_{min})] * [(T_{max}-T)/(T_{max}-T_{opt})]^{bt}\}$$

$$bt = (T_{max} - T_{opt})/(T_{opt}-T_{min})$$

$$f_{VPD} = min\{1, max\{f_{min}, ((1 - f_{min}) * (VPD_{min} - VPD)/(VPD_{min} - VPD_{max})) + f_{min}\}\}$$

$$f_{light} = 1 - exp((-light_a) * PFD)$$

The model simulates the effect of phenology, irradiance, temperature, vapour pressure deficit on stomatal conductance. The factors that cause the limiting of the ozone uptake were VPD, soil moisture, and phenology. The limiting effect of VPD is very clear since, high VPD result in stomatal closure which tends to co-occur with high ozone concentrations. High soil moisture deficits also result in reduced stomatal conductance(Emberson et al. 2000).

Chapter 2

Materials and Methods

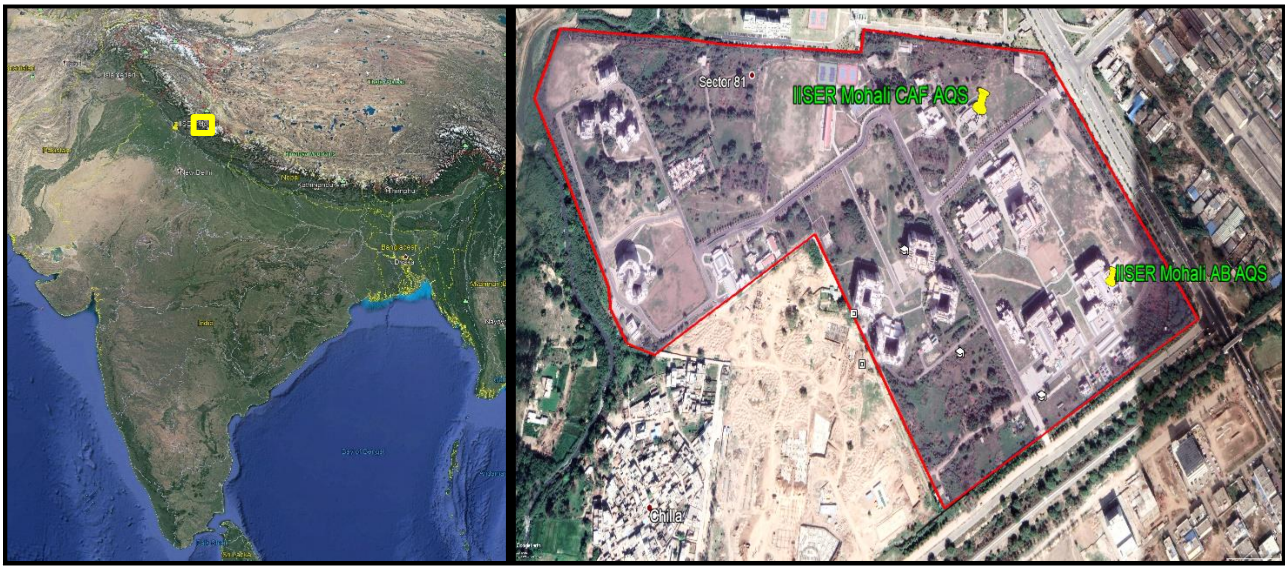

Figure 1: Left, location of Mohali in Indian sub-continent; Right, IISER campus area and Locations of Ambient Air Quality Stations with the campus.

2.1 Site Description

IISER Mohali campus is located in Mohali district where all the experimental, ambient measurements and analytical work was carried out. Mohali district has hot and dry summers with maximum temperature touching 45ºC, and a dry cold winter with minimum temperature touching 2ºC. The rainy season starts in July and ends in September.

Institute campus cover 125 acres of land with more than 1500 residents. Two Ambient Air Quality Stations have been set up within the campus as seen in figure 1, first AAQS was set in Central Analytical Facility (CAF), 15m above ground since 2011 and the second was setup on top of Academic Block (AB) – II, 40m above ground since summer 2019. Both the AAQS's have Ozone, CO, NOx, SO_2 analysers along with met stations. AB AAQS has Ecotech analysers whereas CAF AAQS has Thermo Fisher's analysers.

Wind sectors are categorised based on directions w.r.t the campus. Chandigarh tricity comprising Chandigarh, Panchkula and Mohali in North-to East sector. Industrial area with thermal power plants in East to South sector and South-Northwest sector is rural residence with predominant agriculture activities. Mobile Decagon met station deployed to get photosynthetically active radiation (PAR), soil moisture.

2.2 NOx Analyser

Alongside my project, smooth functioning and maintaining good data quality of NOx analysers was my responsibility. I have cross calibrated several calibration gas bottles that the station has worked with so far and have performed secondary QA/QC of all the NOx measurments done from August 2011 to December 2019.

NOx measurements

Thermos Fisher's Model 42i chemiluminescence NOx analyser is used to measure ambient concentrations of NO, NO_2 in CAF AAQS and Ecotech's Serinus 40 chemiluminescence NOx analyser is used to measure ambient concentrations of NO, NO_2 in AB AAQS. Both analysers have same measurement principle but internal assembly is uniquely developed by each company.

Principle and working:

NOx analysers operates on the principle that when nitric oxide (NO) and ozone react a characteristic luminescence is observed. This luminescent light is linearly proportional to concentration nitric oxide. As the electronically excited molecules of NO_2 decay to lower state energy, light emissions occur. This technique detects NO based upon the light emitted from chemical species during the measurement, hence called chemilumeniscence. Specifically:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

To measure nitrogen dioxide (NO_2) with chemiluminescent reaction, it must be converted to NO. This NO_2 to NO conversion is done by a heated molybdenum NO_2-to NO at around 325 °C. However, this converter can at times convert other species to NO as well. Hence the analyser measures NO_2*. The detection limit for both the instruments is 150 pptv.

Since it is a highly sensitive instrument that measures trace level gases, it is important that dust or particulate matter doesn't enter the internal system of the instruments. A 0.45 micron filter is attached with a filter holder at the sampling inlet of Thermo NOx analyser while the Ecotech's NOx analyser has a filter holder placed inside the instrument to put the filter before the measurement setup starts. The most common problem that occurs in the Thermo NOx analyser is that the flow controlling capillaries, with inner diameter of 0.2 and 0.5 mm, are blocked. These are very delicate but most problematic part of the instrument. The 0.5 mm capillary can be cleaned with a thin wired whereas the 0.2 mm requires a hair to clean. This blockage are identified with help of two parameters, first is the sample flow drops and the instrument may or may not give an alarm based on the density of the block.

Internal flow diagram of Model 42i NOx is shown in Figure 3, and Serinus 40 NOx is shown in Figure 2.

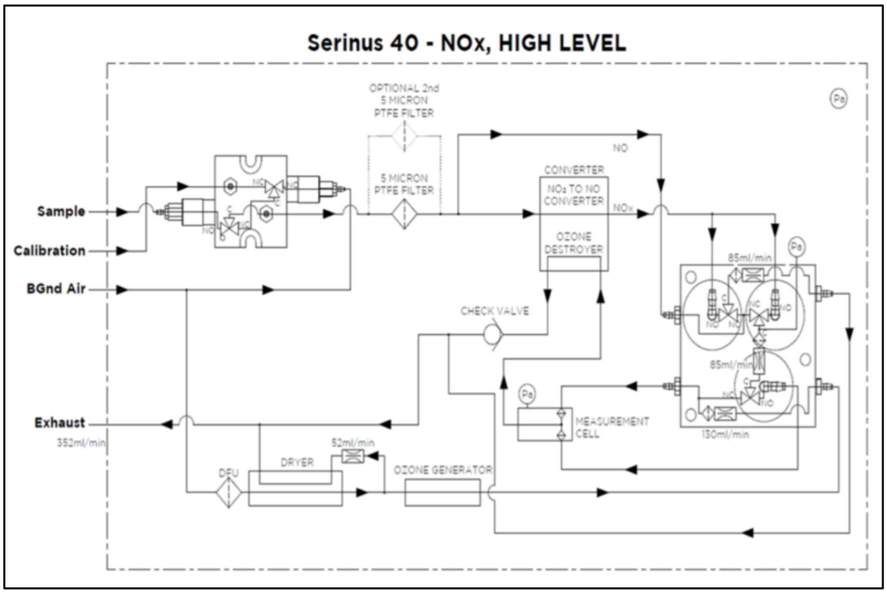

Figure 2: Serinus 40 NO-NO2-NOx analyser internal flow diagram

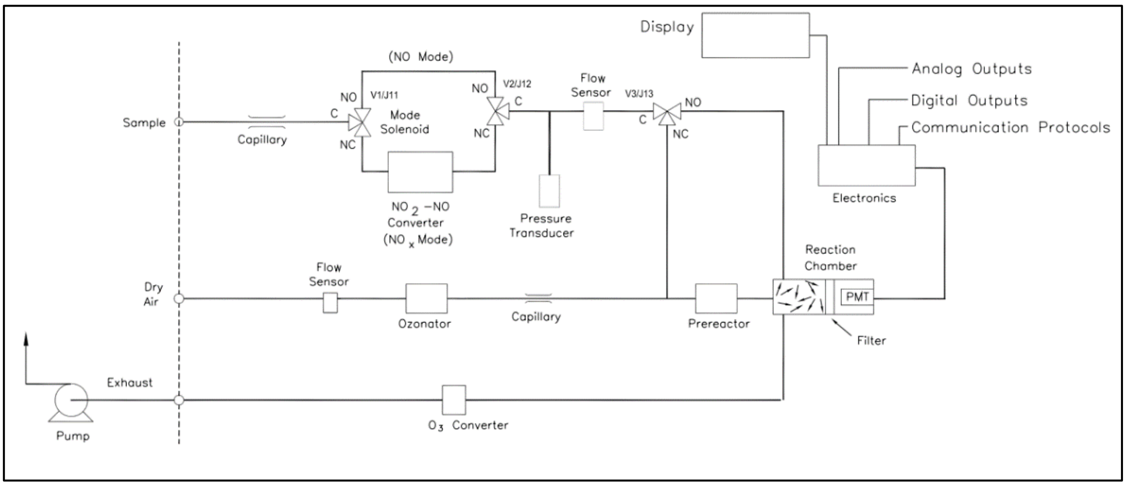

Figure 3: Model 42i-TL Chemiluminescence NO-NO2-NOx analyser internal flow diagram.

Calibration:

Periodic calibration experiments are carried out to ensure good data quality. NO gas is diluted with Zero air using Mass Flow Controllers (MFCs) to introduce 5 different concentrations (within ambient operating range) in the analyser and responses by the instrument are recorded. Before the calibration experiment, zero value is calibrated by passing zero air.

A response v/s introduced graph is plotted shown in Figure 4. Ideally the slope of this graph should be 1 but the instruments lose their sensitivity with time so the slope from calibration experiment is used to adjust instruments sensitivity.

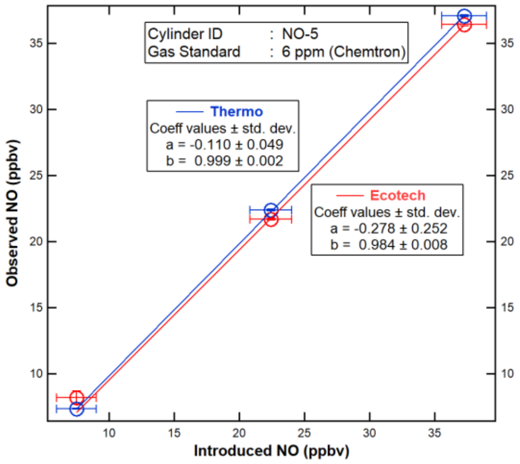

Figure 4: NO calibration graph

The errors or uncertainties while introducing the known conc. arise from the instrumental uncertainty of MFCs used and the uncertainty in NO gas standard.

2.3 Leaf Porometer

To measure the measure the stomatal conductance or water vapour flux from the stomata of the leaf, Decagon Device's SC-1 Leaf Porometer has been used. This instrument has an uncertainity of 10%, but compared to other instruments on the market for measuring stomatal conductance it is portable. Other instruments have several additional functions and some have very low uncertainity but are very inconvenient to carry around in field for measurements.

Principle and working:

Stomatal conductance is defined as the passage rate of water vapour or carbon dioxide through the leaf's stomatal pores. Stomatal conductance depends on size, density of stomata on leaf surface and the degree of opening of stomata.

Leaf porometer arranges the conductance of leaf and series two known elements conductance, to measure the leaf's stomatal conductance. Water vapour flux can be calculated by measuring the difference in relative humidity between the known conductance elements. The humidity at 3 points (inside the leaf and at both the RH sensors) is measured.

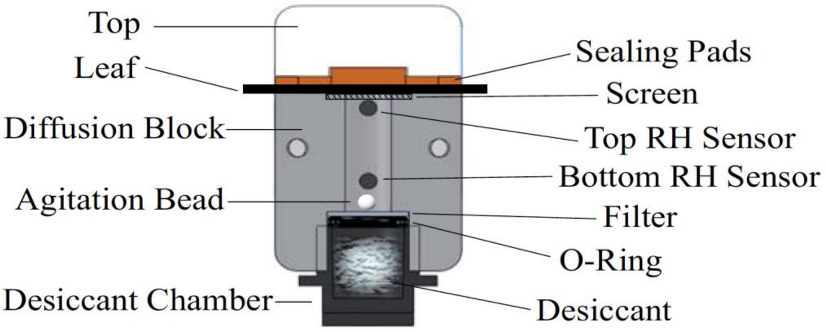

Figure 5: SC-1 Leaf porometer sensor head

Leaf porometer measures the resistance between the leaf and top (1) sensor and the top (1) and bottom (2) sensor as shown in fig. 5.

Vapour flux along diffusion path between nodes 1 and 2.

$$F_{vapor} = g_{d2}(C_1 - C_2)$$

$$C_i = \frac{h_r e_s(T_a)}{P_{atm}}$$

here h_r is the rel. humidity, $e_s(T_a)$ is saturation vapour pressure at T_a temperature of air and atmospheric pressure P_{atm}. Now, g_{d2} is given by,

$$g_{d2} = \frac{\rho D_{vapor}}{d_2}$$

here ρ is the molar air density and D_{vapor} is water vapour's diffusivity.

$$\rho = 446\frac{P_a}{101.3}\left(\frac{273.15}{T}\right)$$

$$D_{vapor}(T, P_a) = 2.12x10^{-5}\left(\frac{101.3}{P_a}\right)\left(\frac{T}{273.15}\right)^{1.75}$$

The final equation becomes:

$$F_{vapor} = \left[\frac{\rho D_{vapo}}{d_2}\right]\frac{1}{P_{atm}}[h_{r1}e_s(T_{a1}) - h_{r1}e_s(T_{a2})]$$

The first assumption is that within the leaf's tissue, relative humidity is 1.0

$$C_{leaf} = \frac{e_s(T_a)}{P_{atm}}$$

Second assumption is that all values of conductivity are in series to maintain constant flux between the two sensors.

Third assumption is that the leaf temperature and the first rel. humidity sensor's temperature are equal. Therefore, the first equation can be rewritten as equation for node at top and for the node at leaf.

$$F_{vapor} = g_{s+d1}(C_{leaf} - C_1)$$

Solving the above equation for series combination of conductance i.e.

$$\frac{1}{g_s + d_1} = \frac{1}{g_s} + \frac{1}{d_1}$$

we finally obtain the equation for stomatal conductance

$$g_s = \frac{\rho D_{vapor}[h_{r1}e_s(T_{a1} - h_{r2}e_s(T_{a2})]}{[e_s(T_{a1})(1 - h_{r1})]d_2 - [h_{r1}e_s(T_{a1}) - h_{r2}e_s(T_{a2})]d_1}$$

In the leaf porometer's sensor head, d1 (= 3.35mm), d2 (= 11.43mm) are the distances.

Measurements and Sampling:

To measure the stomatal conductance of leaves few steps and precautions need to be followed:

1. Thermal equilibrium must be achieved with the environment by the instruments sensor head. To achieve thermal equilibrium the sensor head must be kept in the measurement environment for at least 10 mins.
2. The sensors' reading should be within 2% of each other to measure conductance accurately. The instrument is designed in such a way that measurements cannot be started until sensors are with 2% readings of each other. To achieve this the diffusion path must be well mixed, so a fluoropolymer agitation bead is used and mixing can be ensured by shaking the sensor head. If either of the sensor reads RH 10% or above before starting the measurement then the desiccant in the desiccant chamber is exhausted and needs to be changed. It is a silica desiccant that absorbs water vapour through a Teflon filter between the diffusion chamber and desiccant chamber.
3. Final step is clamping the sensor head onto the abaxial side to start the measurement. This can be tricky with leaves that have curvy edges (e.g. leaves False Ashoka), sometimes the leaf is folded while clamping, this was dealt by discarding the reading and choosing another leaf.

Three trees planted alongside a footpath inside the campus were chosen for sampling. 3-5 leaves with sunlight on them were randomly selected on each tree to measure the stomatal conductance every hour. Hourly averages were taken for analysis as the measurements were scattered over the hour and it is the minimum resolution taken by the DO_3SE model.

Calibration:

Calibration of the instrument is done with a filter provided which diffuses 240 mmol m^{-2} s^{-1} water vapour. The instrument has an auto-calibration function where conductance of the filter is measured and RH sensors are adjusted internally. Once auto-calibrated instrument's sensitivity would hold for few months at least, so another auto-calibration would be required if operating temperature changed by 15ºC. Conductance of the calibration filter were measured every day the leaf porometer was used and were regularly analysed to check the sensitivity. Procedure for auto-calibration includes first two step mentioned in the measurement section, next the filter is wet with 1-2 drops of mille-Q water and placed on calibration plate and the sensor head is clamped onto this plate. The calibration number will be set by the instrument (the leaf porometer) if it measures 3 consecutive measurements all within 7.5% of each other else it will prompt for another measurement until the criteria is met.

2.4 Dynamic Branch Cuvette

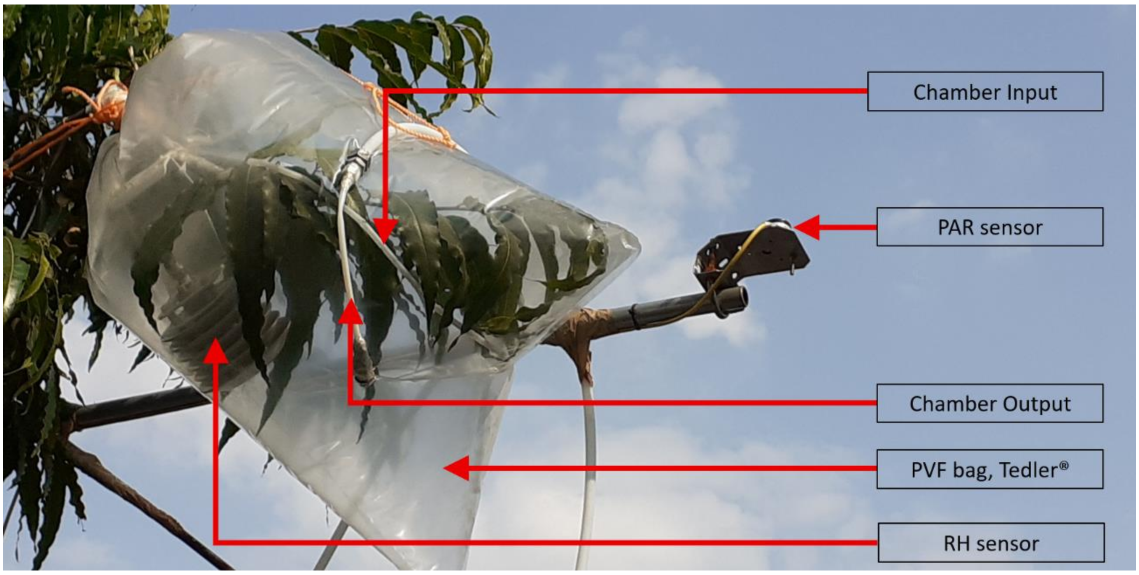

Figure 6: Dynamic Branch cuvette set on *Polyaltheia longifolia*

A branch with continuous solar radiation on it during day time was selected for False Ashoka tree. Transparent polyvinyl fluoride bag (by Tedler®) was used as a chamber around the branch with an input and output hole for controlled air flow. To pump air through the cuvette two heavy duty pump were used, one for input flow and another for suction at output, with a flow rates of 30L/min. the tubing length were adjusted to ensure sufficient air flow through the chamber to ensure that the chamber did not shrink in size and walls didn't touch the branch or explode due to imbalance of flow between the input and output pump. Zero air was input to the chamber and laminar flow was ensured. Zero air implies air parcels should not contain VOC and it should be dry. To generate zero air ambient air was first passed through a silica filter which absorbs water vapour and after which it was passed through a charcoal filter to absorb ozone, NOx and hydrocarbons. The chance of particulate matter in the air could not be dismissed, for which filter of 0.2 micron was placed at the ambient air suction end. The output air from the chamber was connected to PTR-QMS which measured the BVOC concentrations and cavity ring down spectroscopy (CRDS) which measured the greenhouse gases concentrations. This dynamic online setup measurements were taken for 3 days. Background measurements were taken 3 times every day. Background measurements were taken to check for VOCs in the zero air that was being passed into the cuvette and these were adjusted in the final emissions. An assumption was made that no VOCs were deposited on the PVF bag. After using the PVF bag for several experiments on different trees, the transparency of the bag would be lost. A RH, pressure, temperature sensor were placed inside the cuvette, such that it did not touch the branch leaves. A RH, pressure, temperature sensor along with a PAR sensor were placed outside the chamber to measure the ambient parameters. RH as shown in figure 6 is a combination RH, pressure and temperature sensors. The temperature sensor inside the chamber is used to calculate chamber's volume.

Emission flux (EF_{BVOC}) was calculated using the following equation:

$$EF_{BVOC}\ (\mathrm{nmol\,m^{-2}\,s^{-1}}) = \frac{m_{out,BVOC} - m_{in,BVOC}\ (\mathrm{nmol\,mol^{-1}})}{V_m\ (\mathrm{m^3\,mol^{-1}})} \times \frac{Q\ (\mathrm{m^3\,s^{-1}})}{A\ (\mathrm{m^2})}$$

here $m_{out,\ BVOC} - m_{in,\ BVOC}$ is the difference between the output and input air's BVOC concentrations, Q is the air flow rate that is being passed in the cuvette system in cubic meters per second, V_m is the gas's molar volume which was calculated using temperature inside cuvette, A is the total leaf area calculated by scanning the leaves after the completing the experiment.

The leaves were plucked after the experiment had ended and were scanned using a scanning machine with 2 hours. These scanned images were used to calculate the total leaf area using ImageJ software. Once the leaves were scanned they were put into hot air oven to dry for 18-24 hours. After 18 hours their weight was measured and few hours which it was measured again. This was repeated until the weight was constant for 2-3 measurements. This weight was used to calculate flux in µg BVOC emitted per gram of leaf per second. Since the units in which BVOC emissions have been reported are nmol BVOC emitted per meter square leaf area per second this unit has been used in the analysis.

Chapter 3

Results and Discussion

3.1 Environmental Response Functions

The maximum and minimum stomatal conductance were calculated by averaging the 99.99 and 0.1 percentile values of stomatal conductance of water vapour respectively. As a result g_{max} and g_{min} (mmol H_2O m^{-2} s^{-1}) were defined as 865 and 17.3, respectively for *Polyalthia longifolia*. The g_{max} and g_{min} ozone uptake amounts to 528.3 mmol O_3 m^{-2} s^{-1} and 11.5 mmol O_3 m^{-2} s^{-1} respectively, uptake for other species is given in table 2. The five parameter values were put into the model and the boundary lines were adjusted according to each parameter for *Polyalthia longifolia* and their parametrizations are listed in table 1.

As shown in figure 6, False Ashoka shows maximum stomatal conductance during its fruiting period which is between July to September (Anon n.d.) at ambient temperatures around 33^{0}C and relatively low VPD. The soil moisture content seems to have no impact on conductance unless soil moisture drops below ~8.5% SM a behaviour the plant possibly owes to the fact that it grows a single tap root that reaches till the water table and hence is not water limited due to the soil moisture measured in the top 20 cm of the soil. The optimum temperature of 33^{0}C appears to be relatively high in comparison to the minimum temperature of 0^{0}C and low when compared to the maximum temperature of 45 ^{0}C. There seems to be a strong difference between the range of stomatal conductance typically observed during fruiting period in monsoon season and the rest of the year, with the conductance values outside the reproductive growth phase not exceeding 50% of $g_{sto\text{-}max}$ at any point in time. The strong behavioural difference between reproductive growth and vegetative growth makes it very difficult to determine the environmental response function to the vapour pressure deficit, as is unclear whether the drop above 1.7 kPa VPD is due to the plant response to VPD or merely due to the fact that higher VPD values were nor observed during the fruiting time of the plant (monsoon season). However, model measurement agreement during summer season improves when VPD max is set to a higher value such a 4 kPa VPD. During vegetative growth no stomatal closure is observed at VPD as high as 7.25 kPa with maximum conductance values still touching 20% of the maximum stomatal conductance even under very dry conditions. Under the same conditions the highest conductance in the early morning hours hardly exceeds 40% of the maximum indicating that it may be a soil moisture related function rather than the VPD that is responsible for determining stomatal conductance. Full stomatal closure due to VPD was not observed within the ambient VPD range but the data seems to suggest that it would only occur at a VPD of 8.5 kPa or more. This ability to sustain a certain amount of photosynthesis even under relatively dry conditions might be due to the fact that the plant has access to sufficient moisture as it taps into the water table. PAR function's $light_a$ parameter was adjusted to α=0.004, a value which indicates that this species adjusts stomatal aperture in response to light till a threshold of 1000 μmol $m^{-2}s^{-1}$. This agrees with the observed data but is different from the value recommended in the mapping manual α=0.016 (CLRTAP (Convention on Long-Range Transboundary Air Pollution) 2017) which represents a low sensitivity to light above a threshold of 200 μmol $m^{-2}s^{-1}$ for all species.

The literature reveals a wide range of values for different evergreen trees ranging from α=0.035 i.e. almost no response to light above a threshold of 100 μmol $m^{-2}s^{-1}$ for *Astronium graveolens Jacq.*(Cassimiro et al. 2016), a moderate sensitivity α=0.014 (Assis et al. 2015) for guava (*Psidium guajava L.)* and a high sensitive for Holm oak (*Quercus ilex*) 0.009 (Alonso et al. 2007). Till date all evergreen tree species studied for their stomatal conductance including the one studied in this present study belong into different families. The strongest sensitivity to light as been found in two deciduous tree species (Hoshika et al. 2020) black alder (*Alnus glutinosa*) and rowan (*Sorbus aucuparia).*

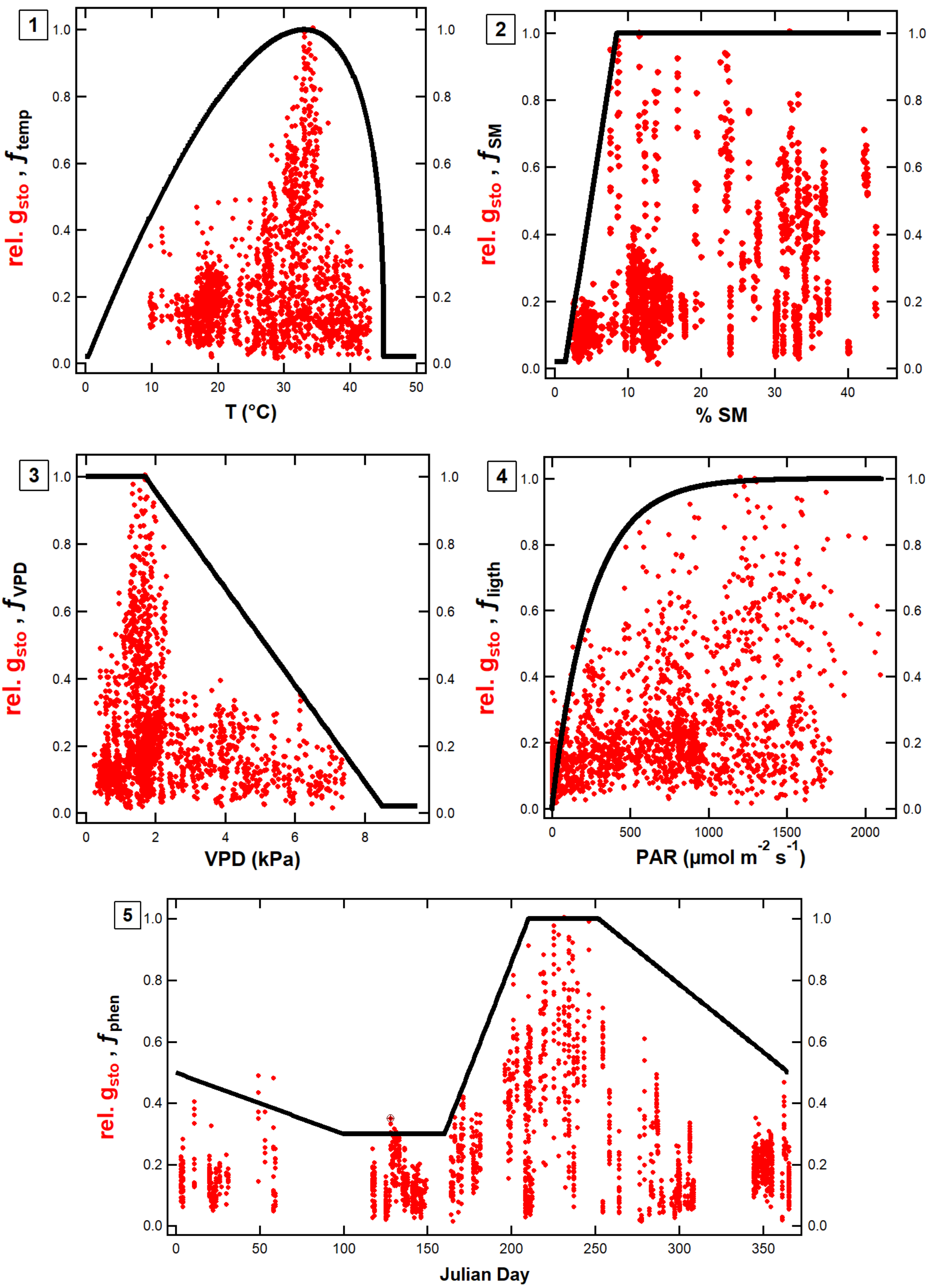

Figure 7: Relationship between g_{sto} expressed as ratio of the species specific maximum and **1** ambient temperature (T, ºC), **2** soil moisture (SM, %), **3** vapour pressure deficit (VPD, kPa), **4** PAR, (µmol m^{-2} s^{-1}) and **5** phenological stage for *Polyalthia longifolia*. Solid line represents boundary lines, the maximum function.

Table 1: DO_3SE model parametrization table for *Polyalthia longifolia* (this study) and other evergreen and deciduous trees studied.

Functions	**Parameters**	**Units**	**g_{sto} parametrization**					
			P. longifolia[1]	***Q. ilex***[2]	***A. glutinosa***[3]	***S. aucuparia***[4]	***V. myrtillus***[5]	***P. guavaja***[6]
	g_{max}	mmol H_2O m^{-2} s^{-1}	865	285	300	240	140	721
f_{min}		Fraction	0.02	0.02	0.13	0.17	0.17	0.026
f_{phen}	Start day	Julian day	0	0	121	121	121	0
	End day	Julian day	365	365	304	304	304	365
	a	Fraction	0.5	1	-	-	-	1
	b	Fraction	0.3	1	-	-	-	1
	c	Fraction	0.1	0.3	0.3	0.3	0.3	0.4
	d	Fraction	1	1	0.3	0.3	0.3	1
	e	Fraction	0.5	-	-	-	-	-
f_{light}	α	Constant	0.004	0.009	0.0024	0.0043	0.0104	0.014
f_{temp}	T_{min}	ºC	0	2	5	0	5	15
	T_{opt}	ºC	33	23	29	23	20	28
	T_{max}	ºC	45	38	40	40	40	43
f_{VPD}	VPD_{max}	kPa	1.7	2.2	1.8	1.2	1.2	1.2
	VPD_{min}	kPa	8.5	4.0	5.7	7.0	4.7	5.5
f_{SM}	SM_{max}	%	8.5	-0.2*	Preset	Preset	Preset	22
	SM_{min}	%	1.5	-4.5*	Preset	Preset	Preset	3

*units in MPa (f_{SWP})

Binomial name(BN), order (O), family (F), genus (G) and species name (S) of these evergreen tropical tree: **1** BN: *Polyalthia longifolia*, O: Magnoliales, F: Annonaceae, G: *Polyalthia*, S: *P. longifolia*; **2** BN: *Quercus ilex*, O: Fagales, F: Fagaceae, G: *Quercus*, S: *Q. ilex*; **3** BN: *Alnus glutinosa*, O: Fagales, F: Betulaceae, G: *Alnus*, S: *A. glutinosa*; **4** BN: *Sorbus aucuparia*, O: Rosales, F: Rosaceae, G: *Sorbus*, S: *S. aucuparia*; **5** BN: *Vaccinium myrtillus*, O: Ericales, F: Ericaceae, G: *Vaccinium*, S: *V. myrtillus*; **6** BN: *Psidium guajuva*, O: Myrtales, F: Myrtaceae, G: *Psidium*, S: *P. guajuva*

Table 1 compares DO_3SE model parametrization of *Polyalthia longifolia* and other evergreen tropical trees as well as to some deciduous trees. While comparing in particular the phenology functions it must be kept in mind that all tropical evergreen trees studied so far were studied in Brazil where the wet season occurs in winter (December-March) rather than in July –September. Hence the reported values for f_{phen} a, b and d tune the model for the same behaviour (maximum stomatal conductance during wet season). In India f_{phen} c and d must be set to 1 and the "start of soil moisture limitation date" must be set to the start of the wet season to trick the model into producing the correct phenology function.

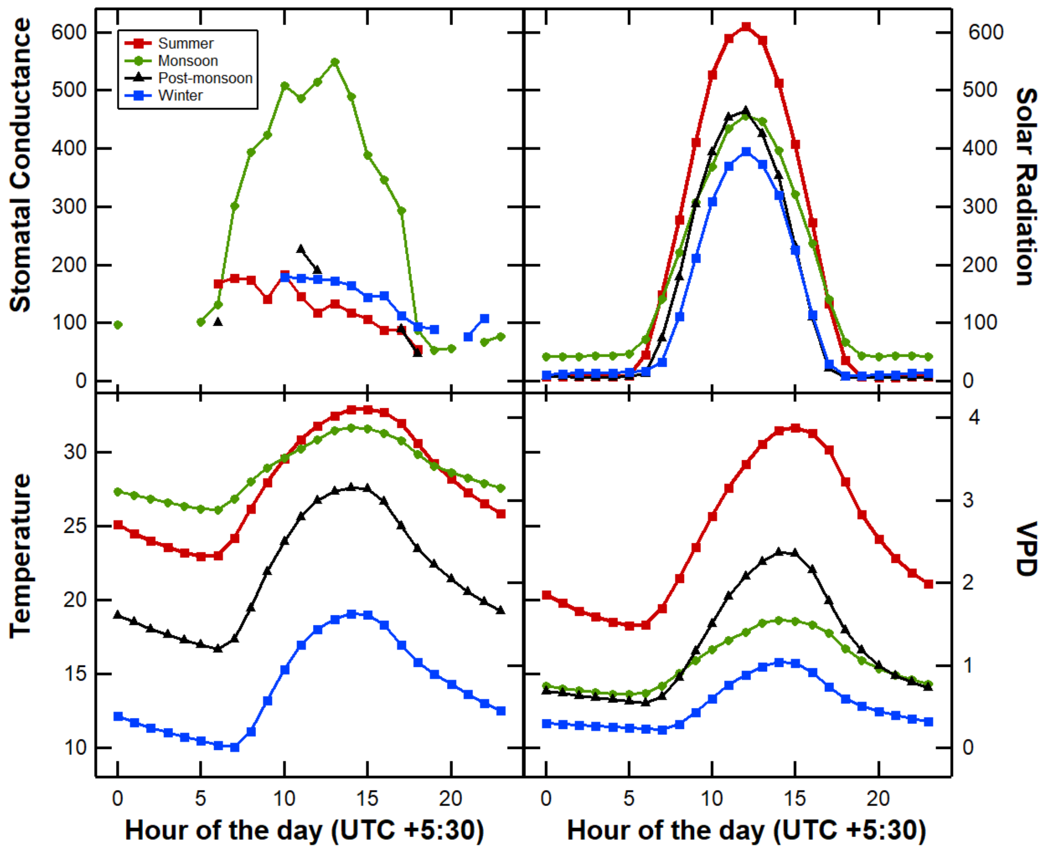

Figure 8: Diel profile for stomatal conductance (mmol m^{-2} s^{-1}) of water vapour for False Ashoka, ambient temperature (ºC), VPD (kPa) and global radiation (W m^{-2}).

Figure 8 shows the diurnals profile for stomatal conductance (mmol m^{-2} s^{-1}) of water vapour for *Polyalthia longifolia* during different seasons. This plot includes observations for all hours of the day where observations have been made on at least three different days during the same season. In addition, the figure shows the typical diurnal profile of ambient temperature (^{0}C), vapour pressure deficit (kPa) and solar radiation (W m^{-2}) during different seasons. The stomatal conductance shows diurnal behaviour with the lowest conductance during night time when solar radiation is zero. However, a conductance of up to 100 μmol $m^{-2}s^{-1}$ is at times observed due to respiration. There is a pronounced difference in the stomatal conductance between wet season, which coincides with the fruiting period of the plant and during the rest of the year. During wet season stomatal conductance peaks during midday when solar radiation peaks. Stomata open with sunrise and close with sunset and aperture appears to be controlled by solar radiation and leaf water potential. During dry season stomatal opening occurs after sunrise and proceeds along a trajectory comparable to that during wet season for the first two hours after sunrise. After that, stomatal aperture stabilizes at the level attained 2 hours post sunrise for some time and decreases throughout the day. This appears to indicate that moisture transport limitations and leaf water potential could be crucial for predicting stomatal aperture in this plant.

Table 2 shows the maximum measured stomatal conductance for water vapour and the maximum calculated stomatal conductance for various other trance gasses. However, stomatal conductance cannot automatically be translated into a flux. A flux from the atmosphere to the plant or from the plant to the atmosphere is a directional diffusion process. The stomatal conductance provides a proxy for the resistance to that diffusion process. The flux is driven by the concentration gradient between the inside and the outside of the plant. Consequently, the water evaporation is driven by the dryness of the outside air. The ozone and NO_2 flux are usually proportional to the conductance as these two species are rapidly removed by the plant. SO_2, NO and NH_3 uptake on the other hand can face resistance as they can be present within the plasma. CO_2 uptake is largely driven by the rate at which photosynthesis removes CO_2.

Table 2: Stomatal conductance of different species at g_{max} and g_{min} for *Polyalthia longifolia.*

Species	g_{max} (mmol m^{-2} s^{-1})	g_{min} (mmol m^{-2} s^{-1})
H_2O	866	17.3
O_3	528.3	11.5
CO_2	554.2	11.0
NO	671.2	13.4
NO_2	542.1	10.8
NH_3	892.0	17.8
SO_2	439.1	8.8

3.2 BVOCs emission

I screened *Polyalthia longifolia* for its VOC emission potential and found low emissions of both monoterpenes (= 0.8 nmol m^{-2} s^{-1}) and isoprene (= 0.3 nmol m^{-2} s^{-1}) as shown in figure 9 which makes this tree highly suitably for roadside plantations. While so far no measurements have been done during reproductive growth and the emissions may be somewhat higher the reported emissions are negligible in comparison to those of other species frequently planted on roadsides such as mahogany (*Swietenia macrophylla* King) a high monoterpene emitter emitting up to 30 and 60 nmol m^{-2}s^{-1} of monoterpenes during vegetative and reproductive growth, respectively (Vettikkat et al. 2020) and poplar (*populous deltoids)* emitting ~25 nmol m^{-2}s^{-1} of isoprene (Guidolotti, Calfapietra, and Loreto 2011).

Figure 10 indicates that False Ashoka emits BVOCs highest when the solar radiation and temperature are maximum during the day which is around mid-day. For the rest of the period it is a non-emitter with emission of both isoprene and monoterpene being below the detection limit.

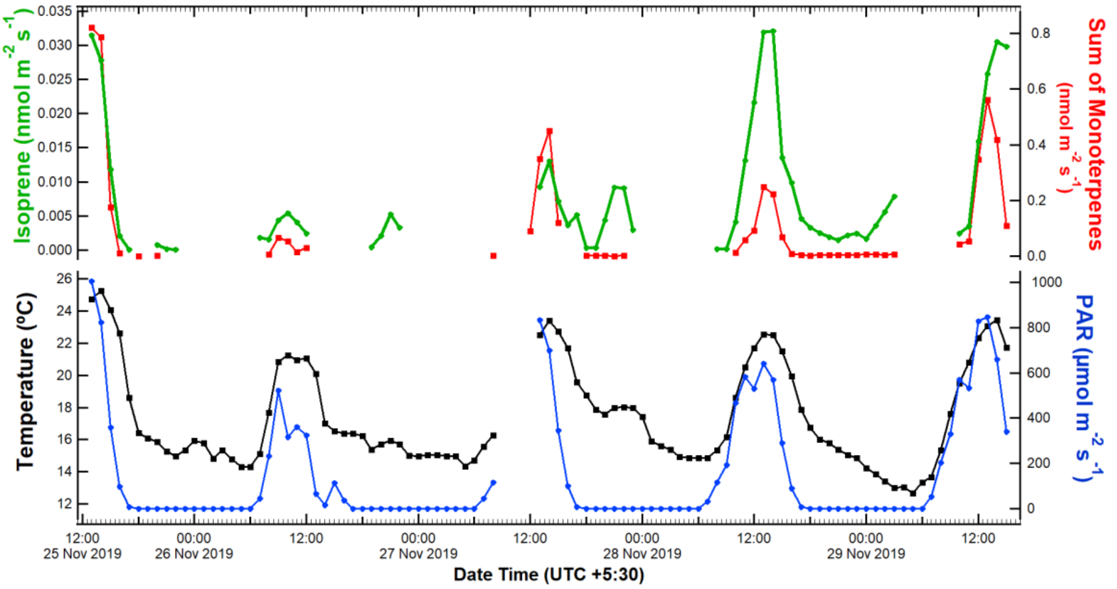

Figure 9: Isoprene and monoterpene emission (nmol of BVOC per m^2 leaf area per sec) of *Polyalthia longifolia* along with PAR and ambient temperature.

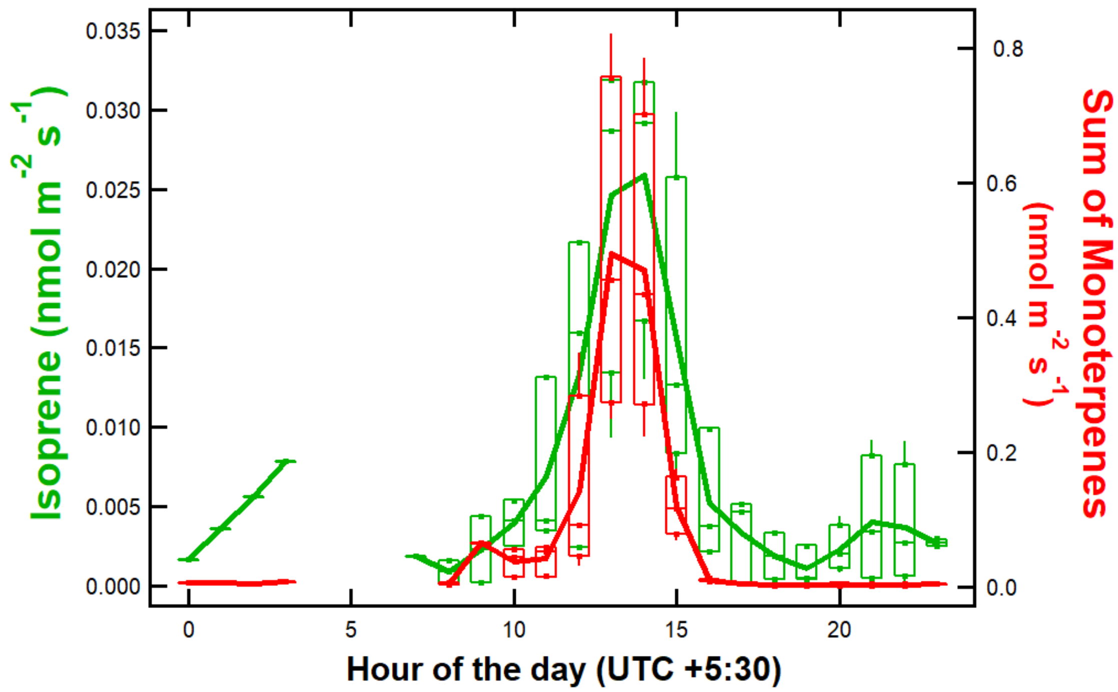

Figure 10: Isoprene and monoterpene diel-profile of *Polyalthia longifolia.*

Chapter 4

Conclusions

Polyalthia longifolia's potential to sustain ozone uptake under extreme conditions such as high VPD, extreme temperatures, extremely dry soil is remarkable. It is a very low emitter of BVOC's which ensures it's low impact on ozone and SOA formation. These characteristics make it an ideal choice for plantation in urban areas where generally the air quality standards are frequently violated. The unique combination of low VOC emission potential combined with the ability to sustain stomatal uptake of ozone and its precursors (NO and NO_2) even during hot and dry conditions make this tree an interesting choice for kerbside locations.

Making urban areas carbon friendly and green has several benefits for their dwellers, but urban greening must be planned and exercised with caution as long they are strong emitters of NOx. According to Forest Survey of India 2019 report, Polyalthia longifolia is one of the top 5 choices in plantation under tree cover outside recorded forest area in 2 states and 3 union territories, despite its growth spanning over the entire nation. It's the need of the hour to study and promote plantation of trees like False Ashoka in urban environments for their sustenance until NOx and other pollutants are drastically reduced from the atmosphere.

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